

IMPROVED MICROWAVE ABSORPTION OF E-GLASS- EPOXY COMPOSITES BY CONDUCTING POLYMER COATED CARBON NANOTUBES

A dissertation submitted
in partial fulfillment of the requirements for the award of the degree of

Master of Science

By

Payel Mondal

(CY14MSCST11010)

Under the supervision of

Dr. Ch. Subrahmanyam



भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

To the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY HYDERABAD


INDIA

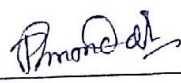
April 2016

Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. Ch. Subrahmanyam**.

In keeping with general practice of reporting scientific observations, due to acknowledgement has been made wherever the work described is based on the findings of other investigators.


Signature of the Supervisor


(Signature)

PAYEL MONDAL
(Student Name)

CY14MSCST11010
(Roll No)

Approval Sheet

This thesis of the project entitled **IMPROVED MICROWAVE ABSORPTION OF E-GLASS-EPOXY COMPOSITES BY CONDUCTING POLYMER COATED CARBON NANOTUBES** by **Payel Mondal (CY14MSCST11010)** is approved for the award of the degree of **Master of Science in Chemistry** from **Indian Institute of Technology Hyderabad** during the year 2015-2016.



Dr. SURENDRAK. MARTHA

Assistant Professor
Department of Chemistry
Indian Institute of Technology Hyderabad

Examiner



-Name and affiliation-

Examiner



-Name and affiliation-

Adviser



-Name and affiliation-

Chairman

Acknowledgement

I would like to express my heartfelt gratitude to my project supervisor **Dr. Ch. Subrahmanyam** for his expert, sincere and valuable guidance throughout my entire M.Sc. project at IIT Hyderabad. I am grateful to him for introducing me to a new area of research. The discussions that I had with him were a major source of learning and helped me to improve my knowledge and communication skills. His guidance and inspiration helped me in all perspective during my project.

I owe my most sincere gratitude to **Dr. M. Deepa**, Head of the department of Chemistry and also a member of dissertation committee, who gave me an opportunity to do this project.

I take this opportunity to express my heartfelt thanks to **Mr. Krushnamurty K.** It was impossible to complete my project without his help and inspiration. His valuable advice, extreme care and extensive discussions in each and every stage have been very helpful for me.

I am grateful to all my lab mates **Chandana L., Laxminarayana B., Subramanyam P., Debjyoti Ray** and **V Ashok Kumar** for their cooperation and generous help throughout my project.

I am thankful to all my professors, my friends, my classmates for giving me the moral support and inspiration.

I would also like to express my heartfelt thanks to my parents whose continuous support and blessings motivated me to do the work.

Thank you very much.

Payel Mondal

(CY14MSCST11010)

Abstract

Enhanced microwave absorbing properties have been achieved using E-glass-epoxy composites by integrating them with conducting polymers (CPs), namely poly(pyrrole) (PPY), poly(aniline) (PANI), poly (ethylene dioxythiophene) (PEDOT) and Multiwalled carbon nanotubes coated by CPs. In order to obtain CP coating on MWCNTs, *in-situ* polymerization of pyrrole, EDOT and aniline was carried out by using dioctyl sodium sulfosuccinate (structure directing agent), ferric chloride (oxidant) and MWCNTs (template). The formation of CP coating on MWCNTs was confirmed by scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA) studies. Different weight % of CP and CP coated MWCNTs were added to the epoxy resin as nano-reinforcement and the entire mixture was used as a matrix to prepare the 2D laminated E-glass-epoxy composites by hand layup method. Microwave absorbing properties of the prepared E-glass-epoxy composites were analyzed using Wave guide measurement. Initial results showed that CP coated MWCNTs, at 0.5wt% addition to epoxy imparted highest microwave absorbing properties in terms of permittivity and reflection loss for E-glass-epoxy composites. CP coated MWCNTs-E-glass-epoxy composites exhibits microwave absorption is mainly due to the dielectric loss of the microwave field in the composites.

Keywords: Polymer-matrix composites; Dielectric properties; Thermogravimetric analysis; Electron microscopy.

TABLE OF CONTENTS

Title	Page no.
1. INTRODUCTION	1-8
2. MATERIALS AND EXPERIMENTAL APPROACHES	9-16
2.1 Raw materials.....	9
2.2 Preparation of conducting polymers.....	10-12
2.2.1 Preparation of PPY.....	10
2.2.2 Preparation of PANI.....	11
2.3 Functionalization of MWCNTs.....	12
2.4 Preparation of CP/MWCNTs.....	13
2.5 Fabrication of E-glass-epoxy-composite.....	14
2.6 Measurement of EM properties.....	15
2.7 Characterization.....	16
3. RESULTS AND DISCUSSION	17-23
3.1 Thermogravimetric analysis.....	17
3.2 SEM analysis.....	18
3.3 Permittivity and permeability.....	19
3.3.1 Permittivity and loss tangent	19
3.3.2 Permeability.....	22
4. CONCLUSION	24
5. REFERENCES	25-28

Abbreviations

RAM	-	Radar absorbing material
EMI	-	Electromagnetic interference
LO Technology	-	Low observable technology
RCS	-	Radar cross section
PMC	-	Polymer matrix composite
CNT	-	Carbon nanotubes
CNF	-	Carbon nanofiber
GO	-	Graphene oxide
ICP	-	Intrinsically conducting polymer
PANI	-	Polyaniline
PPY	-	Polypyrrole
SE	-	Shielding effectiveness
DGEBA	-	Diglycidyl ether of bisphenol – A
DETDA	-	Diethyltoluenediamine
CP	-	Conducting polymer
PEDOT	-	Poly(3,4-ethylenedioxythiophene)
MWCNT	-	Multiwalled carbon nanotube
AOT	-	Dioctyl sodium sulfosuccinate
THF	-	Tetrahydrofuran
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis

List of figures

Figure No.	Description	Page No.
1.a.	Different Radar Frequency Bands within the Range of 1-20 GHz.....	3
1.b.	Stealth Technology: Reflection of Radar Signals from the Target Body.....	4
1.c.	Role of nano-reinforcement for a better binding between matrix and micro-reinforcement.....	5
1.d.	Schematic representation of EMI shielding mechanism.....	8
2.2.1.a.	Synthesis of Poly(pyrrole).....	11
2.2.2.a.	Chemical synthesis of Polyaniline (emeraldine salt).....	12
2.3.a.	Acid functionalization of MWCNTs.....	13
2.4.a.	Preparation of conducting polymer coated MWCNTs.....	14
2.5.a.	Schematic diagram of step wise procedure for fabricating composites.....	15
3.1.a.	TGA plots of COOH-MWCNT, PPY, PANI, PPY/MWCNT and PANI/MWCNT.....	18
3.2.a.	SEM images of (a) PANI (b) PPY (c) PANI/MWCNT (d) PPY/MWCNT.....	19
3.3.1.a.	Real part of complex permittivity of E-glass-epoxy composite with different wt% of CPs and CP/MWCNTs in X – band.....	21
3.3.1.b.	Variation of loss tangent with different CPs and CP/MWCTs.....	22
3.3.2.a.	Real part of permeability of E-glass-epoxy composite at 0.5 wt% of CPs and CP/MWCNTs in X – band.....	23

1. INTRODUCTION

Materials can be categorized into following classes:

- Metals
- Ceramics
- Polymers
- Furthermore, different kind of materials can be integrated or combined together to design a composite material.

Metals lose their strength at elevated temperatures and also heavier in weight. Polymer materials alone are not able to withstand higher temperature as well and get melted at raised temperatures. Ceramic materials exhibit greater ability to withstand higher temperatures, strength and thermal expansion properties, but because of their brittleness, they cannot be used as prime materials for structural purpose. These very problems lead to the exploration of composites ^[1]. Composite is a multiphase material made up of a continuous phase called as the matrix and discontinuous phase called as the reinforcement. Composites generally exhibit significant proportion of properties of both the constituent phases. Some of the natural composites are wood (composed of cellulose fibers and lignin matrix), animal body (bone fibers and tissues as matrix), bone (inorganic and organic components) etc.

Composite materials have attracted magnificently high popularity because of their lighter weight, appreciably good conductivity, high specific strength and stiffness ^[2]. Now-a-days the research on microwave absorbing property of the composites has taken a leap due to their broad applications in aerospace and defense sector in terms of low detect ability (Radar absorbing materials) and increased survivability ^[3]. These very properties have opened a new arena with a wide variety of

applications in recent technology, as well as telecommunications and electronics ^[4]. Microwave absorbing materials are composed in such a way that they could exhibit electromagnetic interference (EMI) shielding and absorption, which make their applicability wider in civil, commercial as well as the military sector ^[5,6].

EMI involves any undesirable, spurious, radiated, and/or reflected signals originated from electrical and magnetic sources that may result some impermissible degradation in work efficiency of equipments ^[7]. It not only affects the normal functioning of electronic instruments, but also it may cause some serious health issues under certain circumstances. Exposure to electromagnetic radiation results such ailments as prostate and breast cancer, miscarriages, leukemia, and Alzheimer's disease ^[8]. The heating of organisms by electromagnetic radiation can be the reason for changing tissues, organs, impulse frequency and blood vessel responses ^[9]. Thus, shielding of EMI is a matter of concern because of their interference with other electronic devices.

Functioning of Modern electronic communication devices involves a broad range of frequencies, which consist of various electromagnetic bands are of individual significances. For instance, the L band (1–2 GHz) exhibits its usage in wireless communication, low earth orbit satellites, etc. the S band (2–4 GHz) operates in multimedia applications such as wireless phones, mobile, television etc.; the C band (4–5.8 GHz) could be implemented for Wi-Fi devices, long distance radio telecommunication; X-band (8–12 GHz) is usually applied for defence tracking, air traffic control, weather monitoring; and the Ku (12–18 GHz) band has its application in very small aperture terminal systems ^[10].

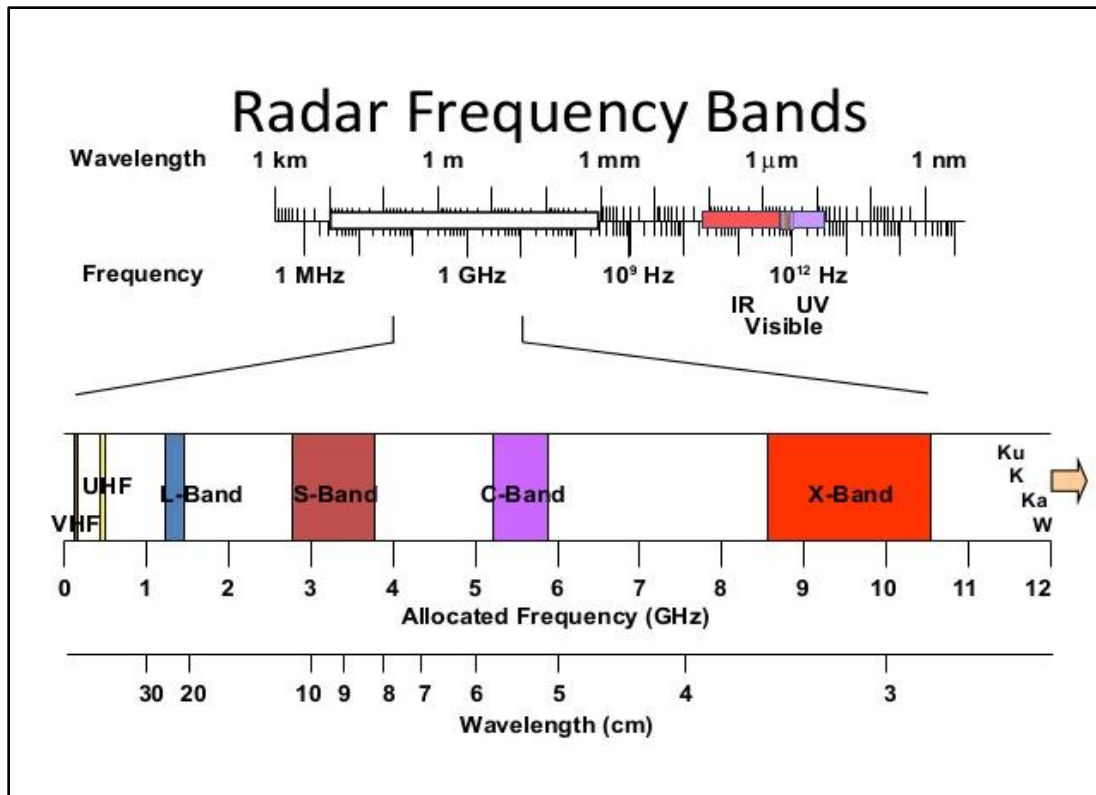


Figure 1.a. Different Radar Frequency Bands within the Range of 1-20 GHz

[<http://www.slideshare.net/J.T.A.JONES/radar-1415354>]

EMI shielding property of a material also plays a vital role in Stealth Technology or LO technology (low observable technology),^[11] which covers a variety of techniques used with satellites, missiles, personnel, submarines, aircraft and ships to make them less visible to sonar, infrared, radar and other detection methods by reducing its Radar Cross Section (RCS)^[12, 13]. No aircraft can be entirely invisible, but the stealth aircraft makes it more difficult for conventional radar to detect or track the object. There are two different ways to make radar invisibility. The object can be shaped in such a way that the incident signal will come and reflect away from the detector radar or the object can be covered with materials that can absorb radar signals.

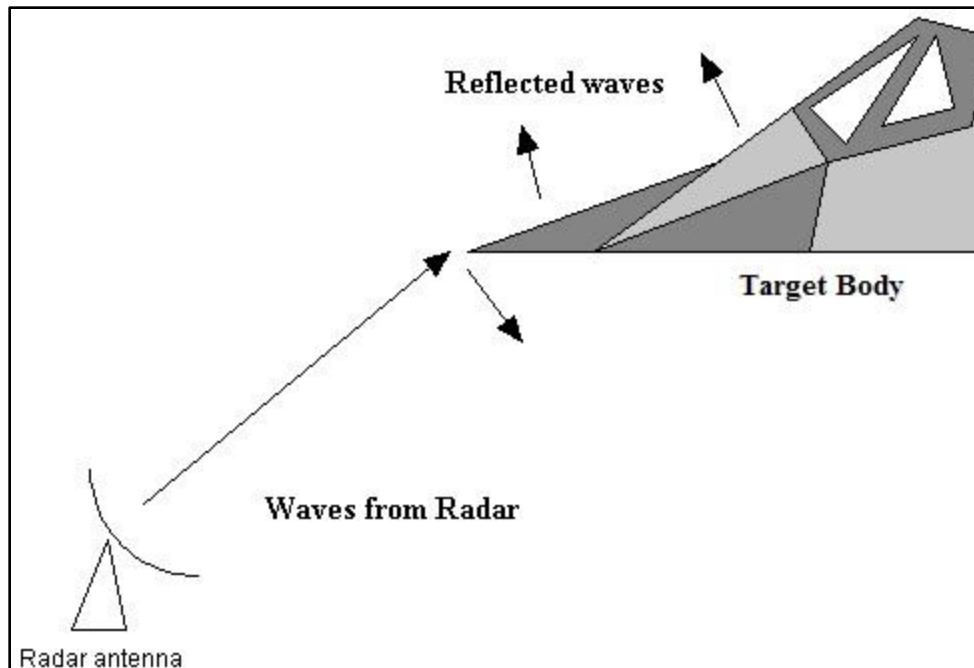


Figure 1.b. Stealth Technology: Reflection of Radar Signals from the Target Body

[http://iron-eagles.tripod.com/articles/passive_stealth.htm]

In order to serve the purpose, polymer matrix composites (PMC) are generally used, where different kind of glass fibers (E-glass, S-glass etc.) are used as micro-reinforcement. But the glass fiber-reinforced composites are almost electromagnetically transparent i.e. they cannot either shield or absorb the electromagnetic radiation efficiently ^[14]. This problem can be overcome by introducing some nano-reinforcements into the polymer matrix. For the fabrication of microwave absorbing composites, epoxy resin is one of the most exclusively used polymers because of its resistance to corrosion, commercial availability, high fracture toughness, irreversible hardening and ease of processing ^[5].

Various nanoparticles are introduced into matrix materials in order to make the composites better performers for EMI shielding because, the two main phases of a composite i.e. matrix and the micro reinforcements don't have enough compatibility to be combined together. During this state

of affairs, nanoparticles with higher active surface composition will act as a binding bridge at the interface ^[15].

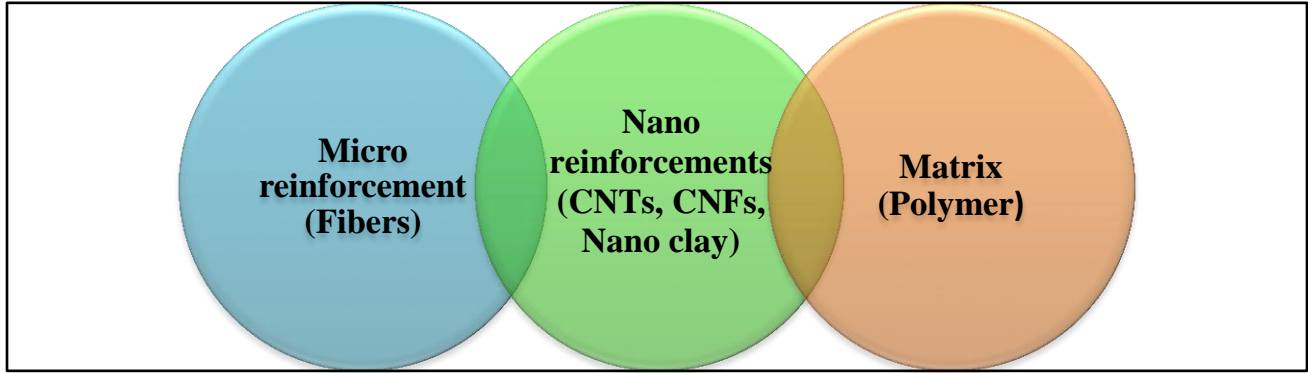


Figure 1.c. Role of nano-reinforcement for a better binding between matrix and micro-reinforcement.

Because of excellent capability of conducting electricity, metals have been conventionally used as electromagnetic interference shielding materials ^[16]. Though, the resistivity of metals increases with increase in temperature, also due to high density, poor resistance to corrosion, and difficulty in processing, metals are not so suitable reinforcements for the fabrication of composites. Carbon based nano-materials reinforced Polymer matrix composites could be prospective substitutes for traditional materials as microwave absorber because of their distinctive combination of electrical, mechanical and thermal properties ^[10]. Among a range of carbon based materials, which can be used as nano-reinforcements are carbon nanotubes (CNTs), graphite, graphene oxides (GO), carbon black and carbon nano fibers (CNFs) etc. Recently, CNTs have been investigated as a promising candidate in order to develop microwave absorbing materials and thus have indicated an avenue to explore the possibility of using other carbon based materials. Exceptionally high mechanical strength, higher aspect ratio and excellent electrical conductivity of CNTs represent high performance in EMI shielding ^[2, 17-25].

Other than carbon based materials, an extensively used nano-reinforcement material for EMI shielding composites is conducting polymer. These conducting polymers may conduct electricity as metals or they can act like semiconductors. The advantages of conducting polymers over metallic conductors are: very high capability to conduct current, very convenient to prepare, low density (e.g. the density of polypyrrole (PPY) and polyaniline (PANI) are 1.2 g/cm^3 and $1.1\text{-}1.3 \text{ g/cm}^3$ respectively, which is comparatively far lesser than that of metallic conductors (8.9 g/cm^3 for copper) and corrosion resistance. They exhibit a unique shielding mechanism of absorption, which differs from metals (shows reflection mechanism) ^[7].

Aside from above discussed nano-reinforcements (carbon based materials and CPs), it has been explored that ferrites kind of materials, e.g. barium hexaferrite, strontium hexaferrite, calcium hexaferrite, nickel ferrite, zinc ferrite, cobalt ferrite exhibit better electromagnetic interference ^[26]. There are several number of dielectric as well as magnetic properties manifested by ferrites and the permittivity (ϵ) and permeability (μ) are most important properties among them.

The recent studies have been focused on the materials to make them more and more efficient for EMI shielding and to achieve the goal, the thought of combining carbon based materials with conductive polymers or ferrite materials have been arisen.

The microwave absorption properties of materials are controlled by a several number of parameters such as,

- Impedance matching between the microwave absorber and free space.
- Specific electric resistance of the composite.
- Frequency response and adaptability of the material in order to function over wide ranges of frequency.

- Dielectric losses and magnetic losses.

At present the research on EMI shielding materials results a wide variety of microwave absorbing materials, but every individual shows its best absorbing capability in a particular range of frequency and under some specific control parameters. Amongst all these parameters, two most fundamental and significant physical quantities are there, upon which absorbing capacity of materials are dependent. One is dielectric losses and second one is magnetic losses. The dielectric losses can be defined by dielectric permittivity and magnetic losses can be defined by the magnetic permeability ^[27]. Being complex quantities, permeability and permittivity are further expressed as the combination of real and imaginary parts. Magnetic permeability (μ) and dielectric permittivity (ϵ) are defined as ($\mu = \mu' - i\mu''$) and ($\epsilon = \epsilon' - i\epsilon''$) respectively where μ' and ϵ' symbolize real parts and μ'' and ϵ'' represent imaginary parts ^[28]. The real parts of permeability (μ') and permittivity (ϵ') account for the extent of polarization in the material and represent the storage capability of the magnetic and electric energy. Complex part of electric permittivity (ϵ'') and magnetic permeability (μ'') correspond to dissipated electric and magnetic energies. The permittivity, which can be observed, is due to electrical conductivity, dipole polarization, electronic polarization and also interfacial polarization. Correspondingly, the dielectric losses are the outcome of dipole relaxation, relaxation of electronic polarization and natural resonances ^[29]. The relation between thickness and magnetic permeability μ is that, the magnetic permeability is inversely related to thickness and this relation further determines that greater the value of μ , lesser is thickness and greater will be the absorption as given by this formula $\text{thickness} = (\lambda / (\mu'' \epsilon''))^{1/2}$ ^[27].

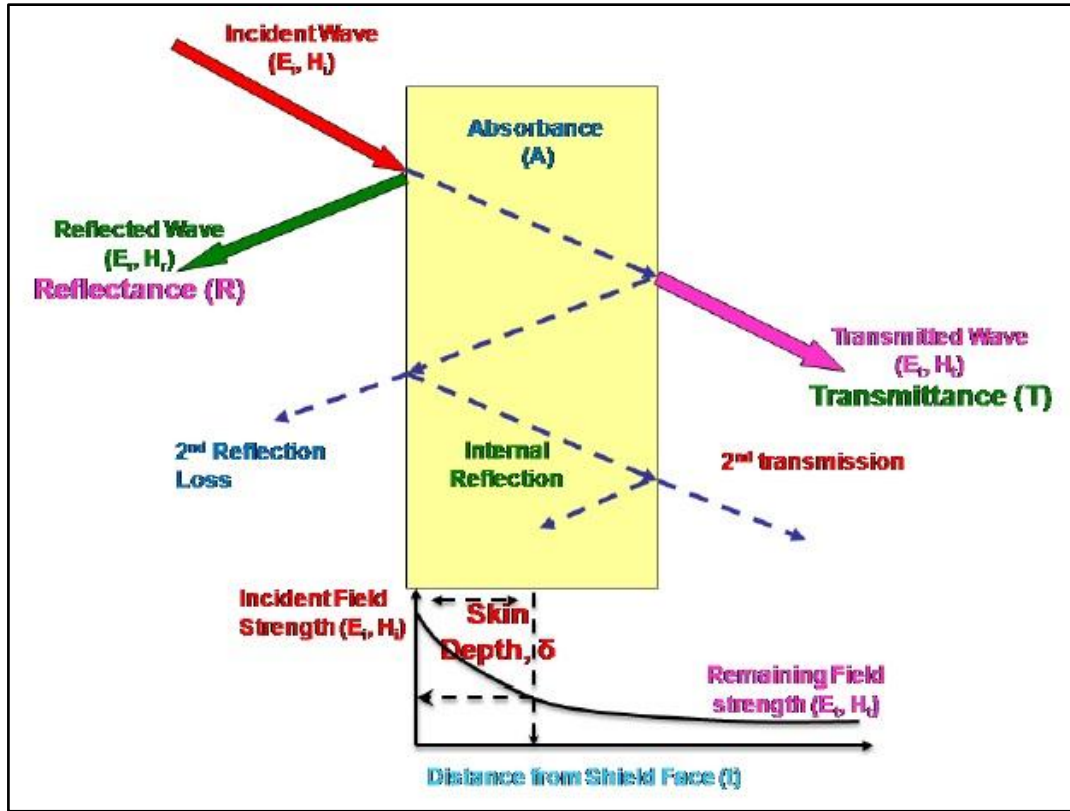


Figure 1.d. Schematic representation of EMI shielding mechanism ^[30]

Shielding effectiveness (SE) of a material is influenced by its magnetic permeability, dielectric attributes, thickness and frequency of the incident radiation. The absorption loss depends on the value of ϵ_r/μ_r , and in order to be a perfect absorber i.e. to attain the maximum absorption loss, $\epsilon_r = \mu_r$. Presence of dielectric and magnetic materials assists in matching of ϵ_r and μ_r which is essential for improving the absorption of electromagnetic waves ^[31]. Also loss tangent is another parameter, which is expressed as the ratio of ϵ'' to ϵ' , measures the amount of energy loss in the material. It has the direct correlation with attenuation factor, which represents conversion of stored energy to dissipated heat. Therefore, the microwave absorption increases with increase in loss tangent, because of the greater attenuation factor.

2. MATERIALS AND EXPERIMENTAL APPROACHES

2.1. Raw Materials:

Epoxy resin (commercial name LY556, Huntsman Advanced Materials (India) Pvt. Limited, Mumbai) produced from epichlorohydrin and bisphenol A along with diamine based curing agent (DETDA, commercial name HY 5200, Huntsman Advanced Materials (India) Pvt. Limited, Mumbai) was used as the matrix phase. E-glass fabric with plain-woven (360 gsm, UTS of 40 GPa) have been used as the main reinforcement. Multiwalled carbon nanotubes (CVD synthesized, procured from M/s Chemapal industries, Mumbai) were used as the nano reinforcement. 98% pure Pyrrole and 97% pure pyrrole and aniline procured from ALDRICH were used as monomers in order to synthesize conducting polymers namely PPY and PANI. 98% pure anhydrous ferric Chloride has been used as an oxidant procured from Qualigens, whereas 98% pure Dioctyl sulfosuccinate sodium salt, a product of ALDRICH, was used as the surfactant. Solvent acetonitrile has been used for washing the formed CPs, was purchased from Sigma Aldrich.

Epoxy resin:

1. Chemical Name : diglycidyl ether of bisphenol A
2. Viscosity : 10,000Cp at 300°C
3. Density : 1.2 g/cc
4. Acid value : 85-120
5. Commercial name : LY-556

Hardener:

1. Chemical Name : diethyltoluenediamine (DETDA)

2. Viscosity : 200 at 25°C
3. Density : 1.0 g/cc

Carbon nanotubes (CNTs):

1. Purity : 99%
2. Metallic impurities : less than 1%
3. Diameter : 100-200 nm
4. Length : 10-20 microns

2.2. Preparation of conducting polymers:

2.2.1. Preparation of PPY:

PPY has been synthesized by *in-situ* polymerization of the monomer pyrrole (PY) following the procedure described in literature, by using dioctyl sodium sulfosuccinate (AOT) as surfactant. Ferric chloride acts as an oxidant here and reverse micro emulsion process is followed for the polymerization. Initially AOT (19.12 mmol) was dissolved in 70ml of n-Hexane, then a solution of FeCl₃ (10.0 mmol) in 1.0 mL of water has been added drop wise to it with constant stirring. The resulting orange-colored mixture was stirred gently and uniformly for 5 min and pyrrole (2.0mmol) monomer has been added to it. After 3 h under moderate magnetic stirring, the black precipitate of PPY was obtained and filtered using suction pump followed by washing with abundant amount of acetonitrile and methanol, the resulting filtrate was then dried under vacuum

[32]

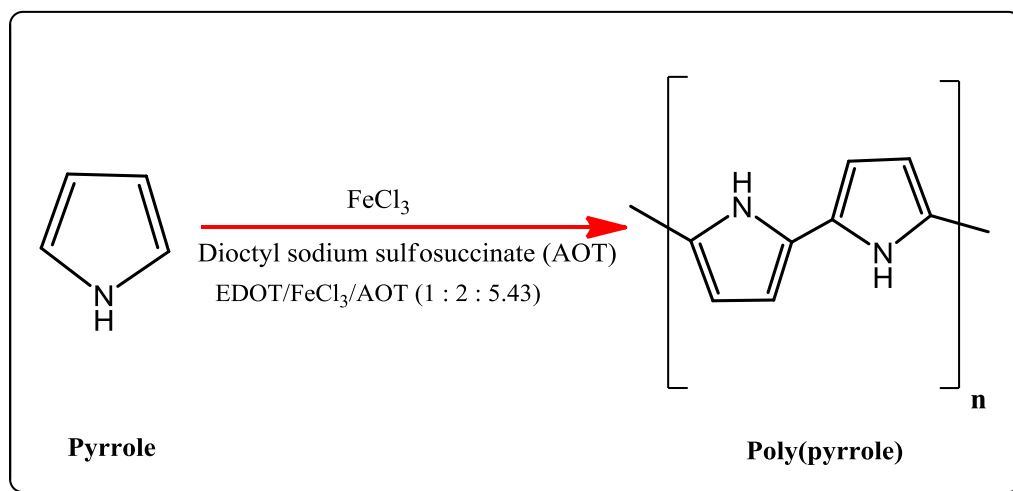


Figure 2.2.1.a. Synthesis of Poly(pyrrole)

2.2.2. Preparation of PANI:

For the preparation of doped PANI, as described in literature, free radical chemical oxidative polymerization process has been followed, through simple procedure, where HCl has been used as dopant. To perform the reaction, initially 0.1mol of aniline has been dissolved in aqueous solution of 1.0M HCl followed by drop wise addition of ammonium persulfate (0.1mol, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100ml distilled water) with constant stirring, which lead to initiation of polymerization. The temperature during the reaction was maintained at 0 ± 0.1 °C. The stirring has been continued for 6 h. The polymer has been obtained in the doped state as dark green colored fine slurry particles. The reaction mixture of PANI was suction filtered followed by washing with abundant amount of water and dried under vacuum ^[33].

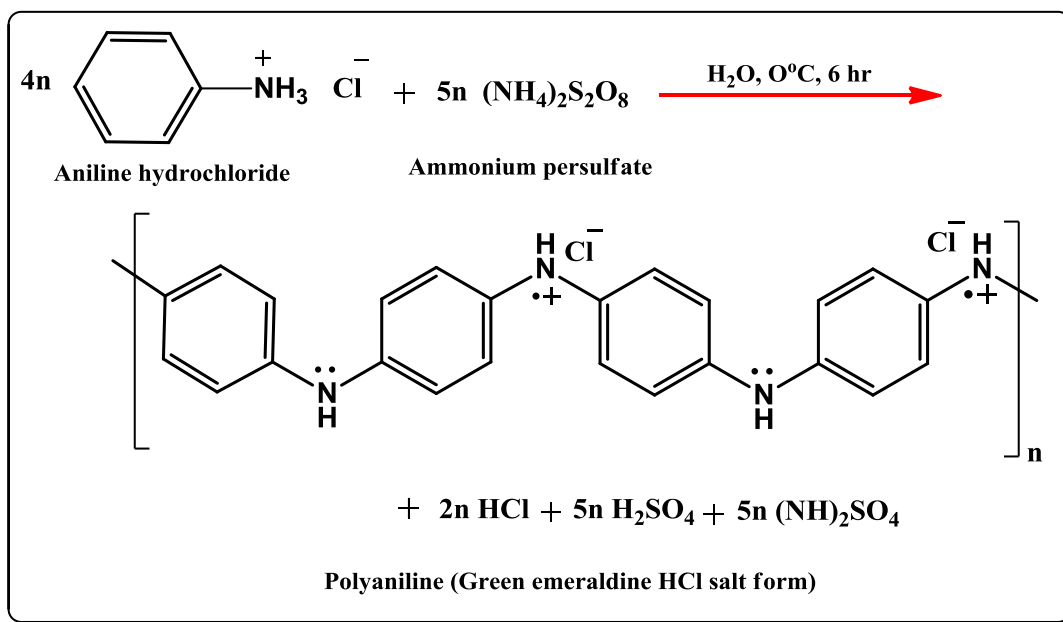


Figure 2.2.2.a. Chemical synthesis of Polyaniline (emeraldine salt) ^[34]

2.3. Functionalization of MWCNTs:

Pristine MWCNTs (2 g) were taken and ultrasonicated in Tetrahydrofuran (THF) at room temperature for 1 hr. After that it has been refluxed at 120°C for 4h with constant and mild stirring and cooled. Then it has been washed with distilled water thoroughly. Unmodified MWCNTs were dispersed uniformly in an acid solution containing concentrated H2SO4/ HNO3 mixture (200 ml) in 3:1 ratio and were refluxed for 24h at 80°C followed by filtration and washing the entire solution with distilled water and acetone until the P^{H} reached at 6-7. The acid modification has been performed in order to exfoliate graphite layers ^[35].

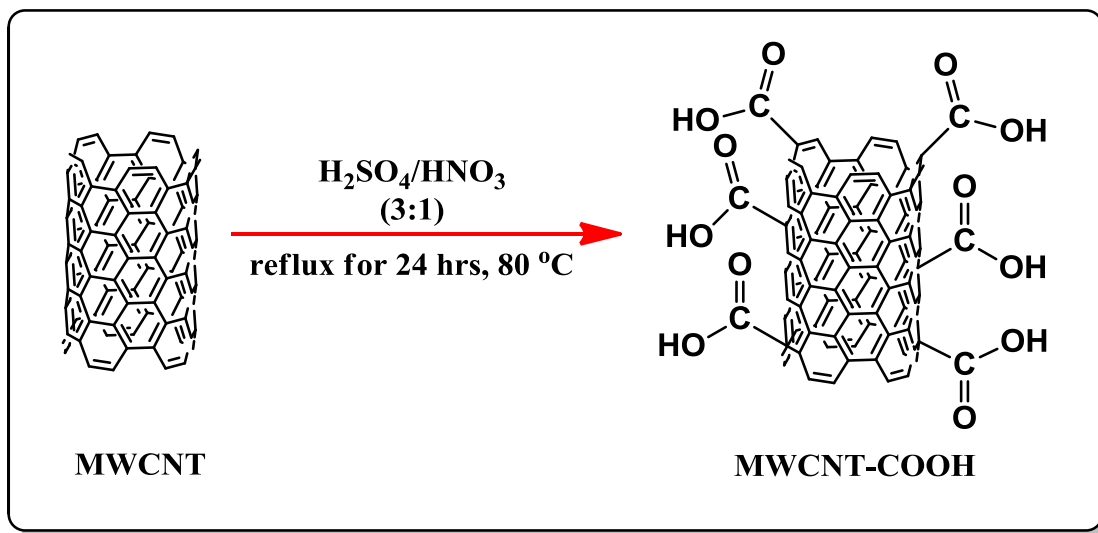


Figure 2.3.a. Acid functionalization of MWCNTs

2.4. Preparation of CP/MWCNTs:

Conductive polymer coated multiwalled carbon nanotubes or carbon fabric have been prepared by functionalization of MWCNTs followed by the formation of CPs on them. First functionalized MWCNTs (MWCNT-COOH) was taken (2 g) in n-hexane (70 ml) and dioctyl sulfosuccinate (AOT) (19.12 mmol) has been added as surfactant. The whole mixture is subjected to constant stirring. Then a solution of FeCl_3 (10.0 mmol) in 1.0 mL of water has been added drop wise to it with constant stirring. Obtained orange-colored mixture was stirred gently for 5 min followed by addition of pyrrole (2.0mmol). 3 hours of constant stirring gives PPY coated MWCNTs. For the synthesis of PANI coated MWCNTs, HCl has been used as dopant and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ acted as an oxidizing agent. The addition of aniline monomer and followed by 6 hours of constant stirring at 0 ± 0.1 °C gives the desired product.

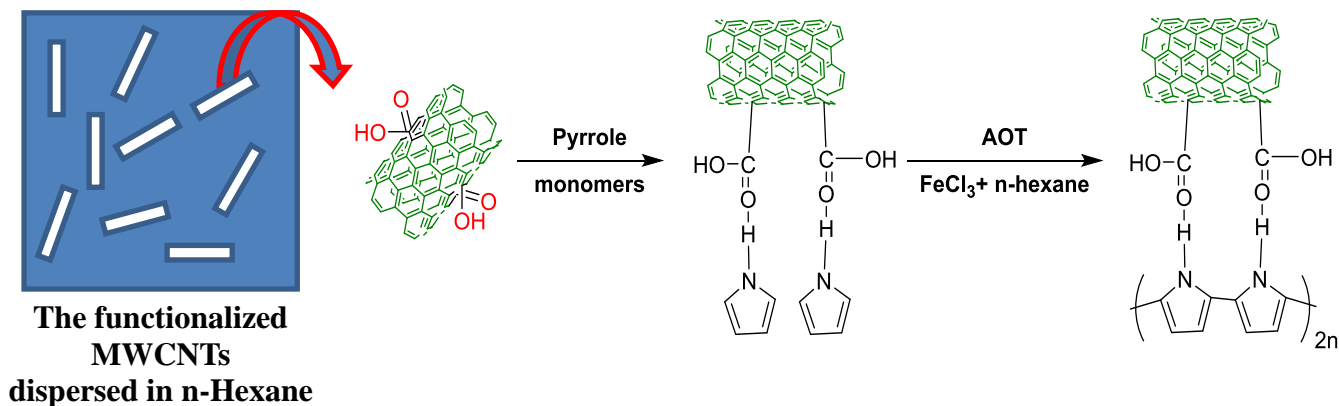


Figure 2.4.a. Preparation of conducting polymer coated MWCNTs

2.5. Fabrication of E-glass-epoxy composites:

Composites have been fabricated by introducing a wide variety of nano-reinforcements. In order to fabricate the composites, initially nano-reinforcement materials (0, 0.5, 1.0 and 1.5wt% with respect to the weight of epoxy resin as required) were dispersed homogeneously in the epoxy matrix by using a ball mill. After 3 hours of ball milling, a hardener or curing agent especially DETDA (24 parts of hardener with respect to 100 parts of epoxy resin by weight) was added to the nano reinforcement-epoxy resin mixture and this mixture was further stirred mechanically for another 15 minutes. Glass fiber was cut into specific dimensions and impregnated with nano-reinforcement dispersed epoxy-hardener mixture using hand layup method. Impregnated fabric layers were stacked and compressed and subjected to curing (heating). Curing was carried out for 1 hour at 70°C, 1 hour at 110°C, 2 hours at 160°C followed by 3 hours at 180 ° C ^[32]. Thus a wide variety of 2D E-glass-epoxy composites have been fabricated using different nano-reinforcements (conducting polymers, conducting polymer coated on MWCNTs) by varying the weight %. Dielectric permittivity and permeability for the prepared samples was measured.

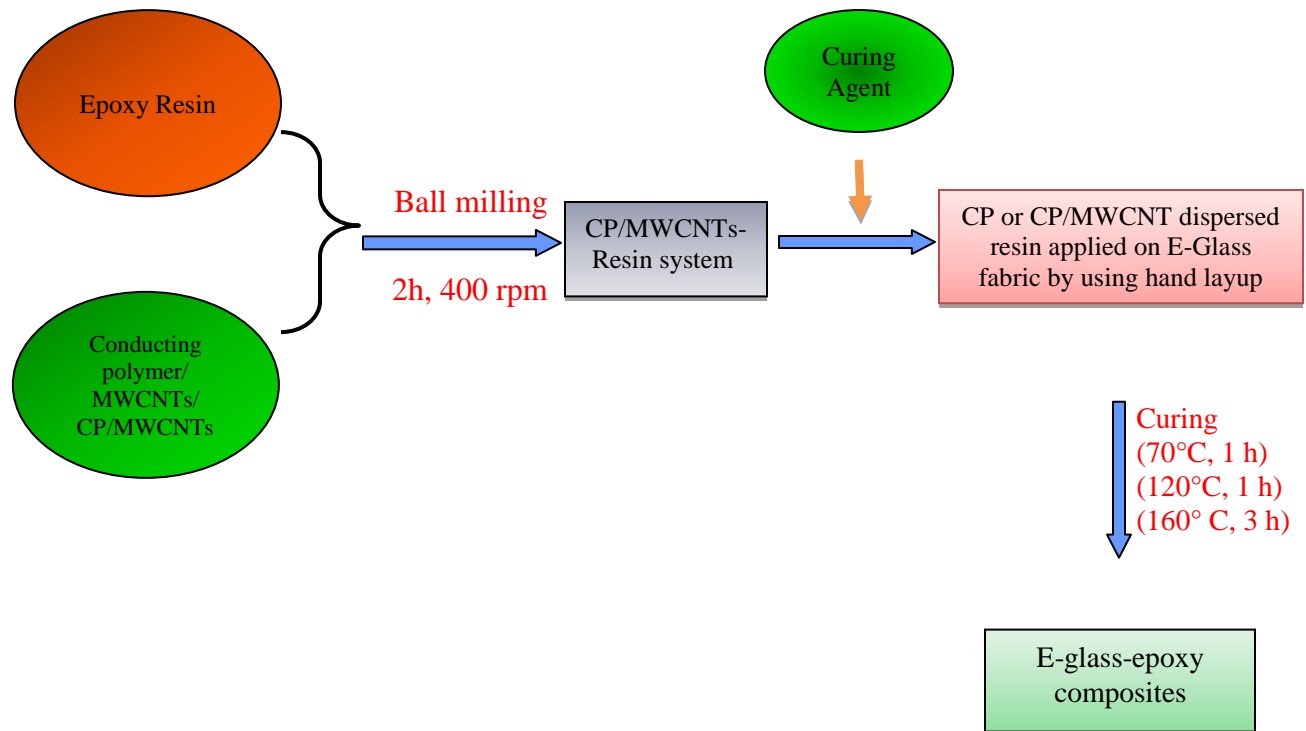


Figure 2.5.a. Step wise procedure for fabricating composites

2.6. Measurement of EM properties:

The composite materials are precisely cut into samples of dimensions 22.86 mm × 10.16 mm (WR 90) for wave guide measurement in order to determine the microwave absorption properties. Complex permittivity values of prepared specimen in the frequency range 8.2- 12.4 GHz are measured through waveguide technique using vector network analyzer (R&S ZVB 20) by employing TRL (Thru, Reflect, Line) calibration. Nicholson-Ross-Weir (NRW) algorithm is used for regressive/iterative analysis as it provides direct calculation of both the permeability and permittivity from S-parameters.

2.7. Characterization:

The thermo gravimetric analysis of the synthesized CPs and CP coated MWCNTs were recorded on TG/DTA, TA Instruments SDT Q600 in air flow from room temperature to 900°C with a heating rate of 10°C min⁻¹. The surface morphologies of prepared conducting polymers, conducting polymer coated MWCNTs and reinforced E-glass-epoxy composites were observed by scanning electron microscope (SEM) (ESEM-FEI Quanta 400, The Netherlands) at an accelerating voltage of 10 kV and magnification of 1000-50000.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric Analysis:

[Fig.3.1.a] showing the thermo gravimetric plots of the individual CPs and CP coated MWCNTs. Polymer/CNTs composites systems exhibit an improvement in thermal stability as compared to the individual polymers. In order to confirm that, thermogravimetric analysis of the PPY/MWCNT, PANI/MWCNT composites has been performed, and the results are depicted in (Fig.3.1.a). MWCNTs possess a very high thermal stability and are stable up to 600°C. Though, pure PPY moderately stable in thermal condition and mass loss occurred in two consecutive steps at around 210°C and 320°C respectively because of its instability in air and nitrogen atmosphere, pure PANI shows decomposition at around 230°C which is ascribed to the thermal decomposition of PPY and PANI chains. Both PPY/MWCNT and PANI/MWCNT composites exhibit more delay decomposition as compared to pure PPY and PANI. The enhanced thermal stability of CP/MWCNT composites can be attributed to some interfacial interaction between CNTs and conducting polymer shell ^[36].

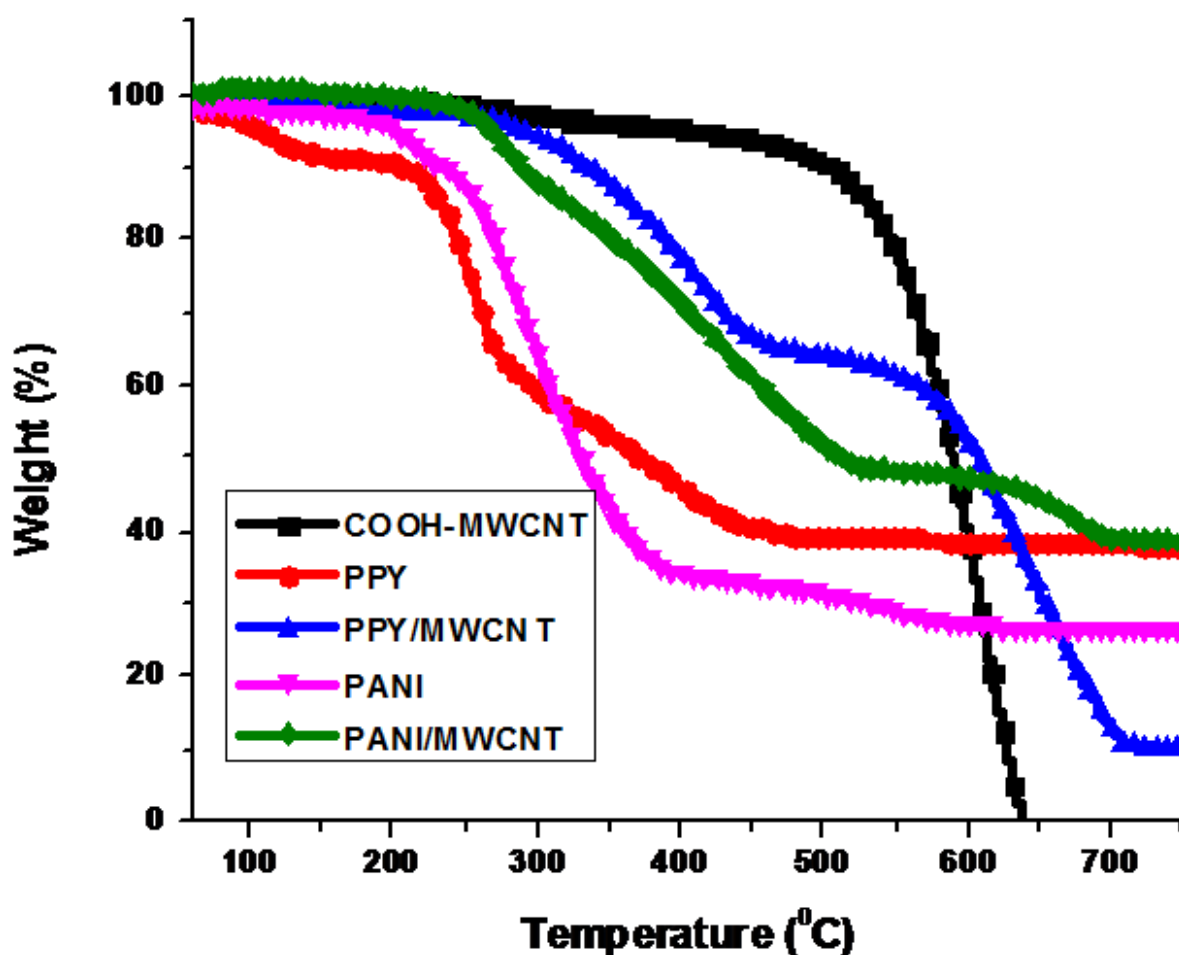


Figure 3.1.a.: TGA plots of COOH-MWCNT, PPY, PANI, PPY/MWCNT and PANI/MWCNT.

3.2. SEM Analysis:

The SEM image of PANI fig. 3.2.a.(a) shows a porous granular morphology, typical of conducting polymer. The SEM image of PPY fig. 3.2.a.(b) shows the existence of interconnected elongated globules with smooth surfaces. The micrographs of both PANI/MWCNT fig. 3.2.a.(c) and PPY/MWCNT fig. 3.2.a.(d) show a network of polymer particles (PANI or PPY)

overlapping with the tubular shapes of MWCNTs. The micrographs indicate that the PPY and PANI coat the MWCNTs fairly well.

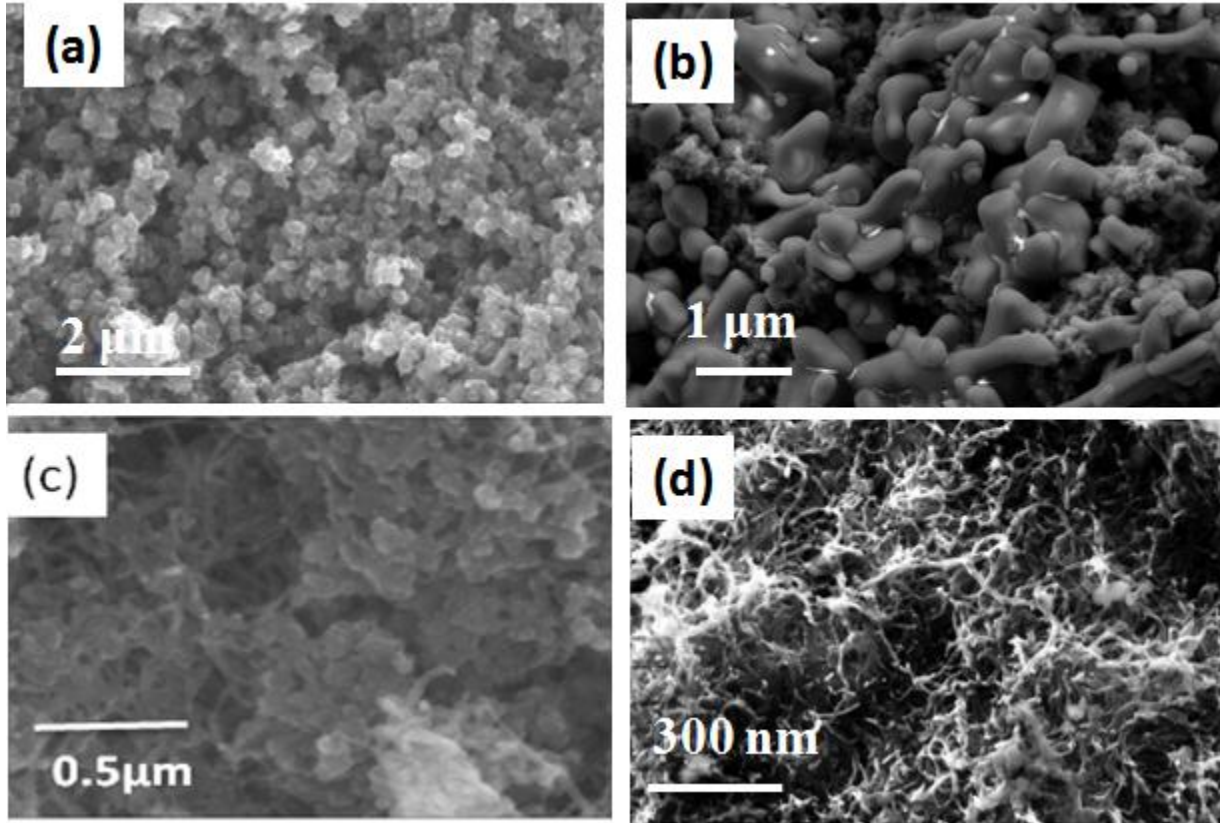


Figure 3.2.a. (a) PANI (b) PPY (c) PANI/MWCNT (d) PPY/MWCNT.

3.3. Permittivity and Permeability:

3.3.1. Permittivity and loss tangent:

Real part of permittivity and loss tangent of E-glass-epoxy composites were measured with different wt % of CPs and CP coated MWCNT and control E-glass-epoxy using waveguide measurement technique are shown in [Fig. 3.3.1.a.] and [Fig. 3.3.1.b.] The real permittivity of the blank E-glass-epoxy composite (without any nano-reinforcement) was 1.8 and that value improved gradually by introducing different wt% of nano reinforcements (CPs and CP coated

MWCNTs (CP/MWCNT). The poor real permittivity of the E-glass-epoxy composite is due to the insulating polymer matrix which resists electron movement or electronic polarization. When a CP/MWCNT is added as nano-reinforcement into the epoxy matrix and the fabricated E-glass-epoxy composite shows that real permittivity increased from 1.8 to 8.7. In the case of blank E-glass-epoxy sample, adjacent glass fibers were divided by an insulating epoxy matrix, which does not favor the process of electronic polarization. Therefore, the Blank E-glass-epoxy shows a lower value of permittivity. When the CP/MWCNT is introduced there in epoxy resin, neighboring adjacent glass fibers allow electron mobility between glass fibers, thus increasing the electronic polarization, therefore real permittivity [Fig. 3.3.1.a] and loss tangent values [Fig.3.3.1.b] are increased. However, the real permittivity or loss tangent attained a maximum value at 0.5 wt% nano-reinforcement, while at 1.0 wt% addition of CP/MWCNT reinforcement, the composite exhibited lower permittivity and loss tangent than the one obtained at 0.5 wt% CP/MWCNT addition and this is attributed to better dispersion of nano-reinforcement into matrix system, a good interfacial bonding between the matrix and fibers may be attained and hence the best permittivity improvements.

The real permittivity of the control E-glass-epoxy, 0.5 wt% PPY-glass-epoxy, 0.5 wt% PANI-glass-epoxy, 0.5 wt% PPY/MWCNT-glass-epoxy and 0.5 wt% PANI/MWCNT-glass-epoxy composites are 1.8, 3.8, 4.5, 8.2 and 8.7, respectively (Fig.3.3.1.a). CP coated MWCNT added epoxy is found to show higher permittivity as compared to PPY or PANI added epoxy. PPY/MWCNT, PANI/MWCNT added composites show higher permittivity than PPY and PANI, due to an efficient π - π stacking between the polymer chains and MWCNT, which facilitates an efficient charge transfer between the CP and MWCNT. Hence, it is concluded that the significant permittivity improvement is due to the non-covalent interactions between the conducting

polymer and MWCNT, which enhances the interfacial polarization. The above results clearly demonstrate that the CP coating on MWCNT is an efficient method to enhance interfacial polarization and to improve the permittivity.

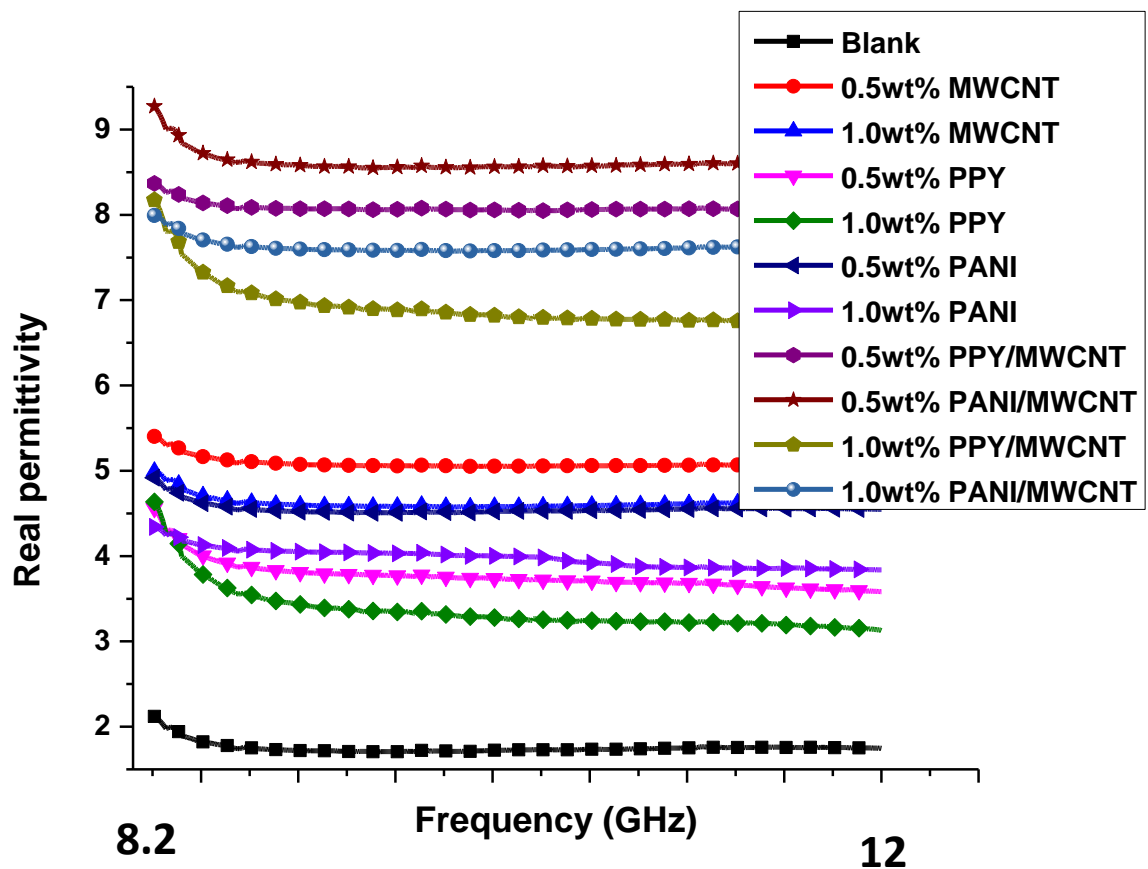


Fig.3.3.1.a. Real part of complex permittivity of E-glass-epoxy composite with different wt% of CPs and CP/MWCNTs in X – band.

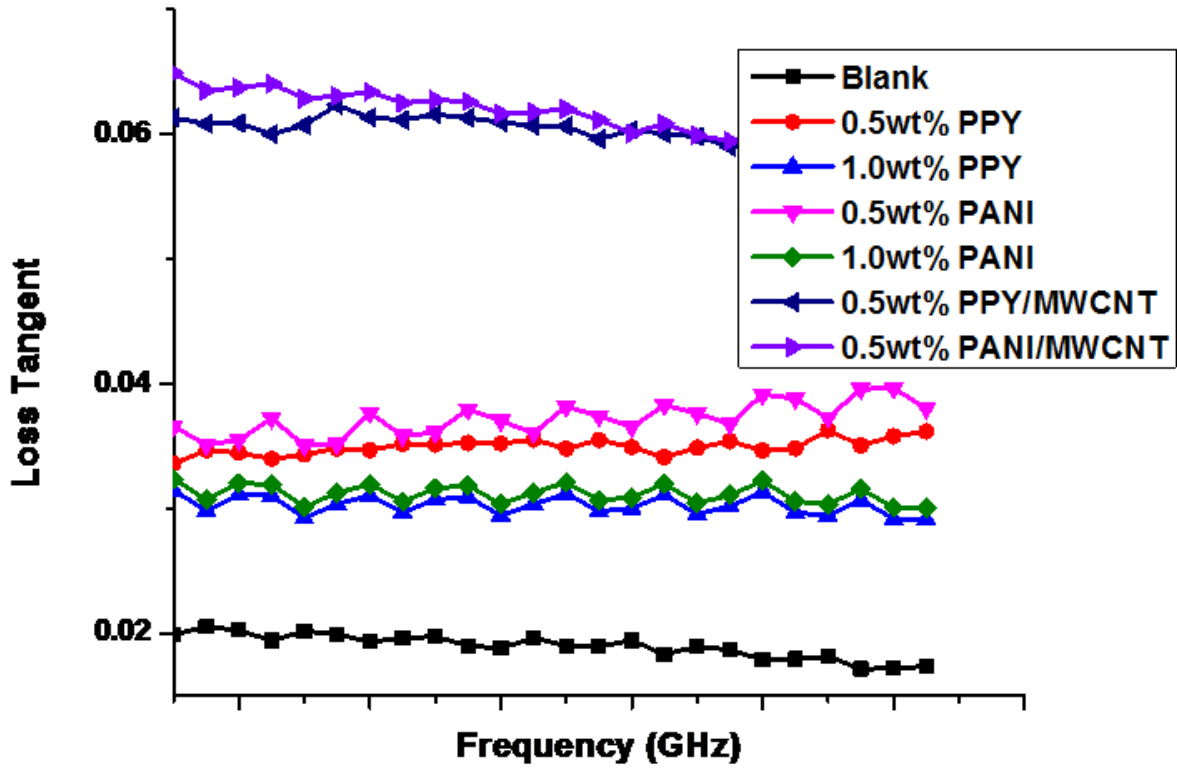


Fig.3.3.1.b. Variation of loss tangent with different CPs and CP/MWCNTs.

3.3.2. Permeability:

Fig. 3.3.2.a shows the real permeability of E-glass-epoxy composites on addition of various nano reinforcements. The real permeability of the control E-glass-epoxy, 0.5 wt% PPY-glass-epoxy, 0.5 wt% PANI-glass-epoxy, 0.5 wt% PPY/MWCNT-glass-epoxy and 0.5 wt% PANI/MWCNT-glass-epoxy composites are 0.73, 0.81, 0.85, 0.92 and 0.97, respectively [Fig.3.3.2.a]. E-glass-epoxy composites having 0.5wt% of CP/MWCNT, exhibits highest permeability than the individual CP added E-glass-epoxy or control E-glass-epoxy composites. This can be attributed to the multiple reflections, which refer to the reflections at various surfaces or interfaces in the

shield and increased interfacial polarization by charge transport capability enabled by the π - π stacking interaction between MWCNTs and conducting polymer chains.

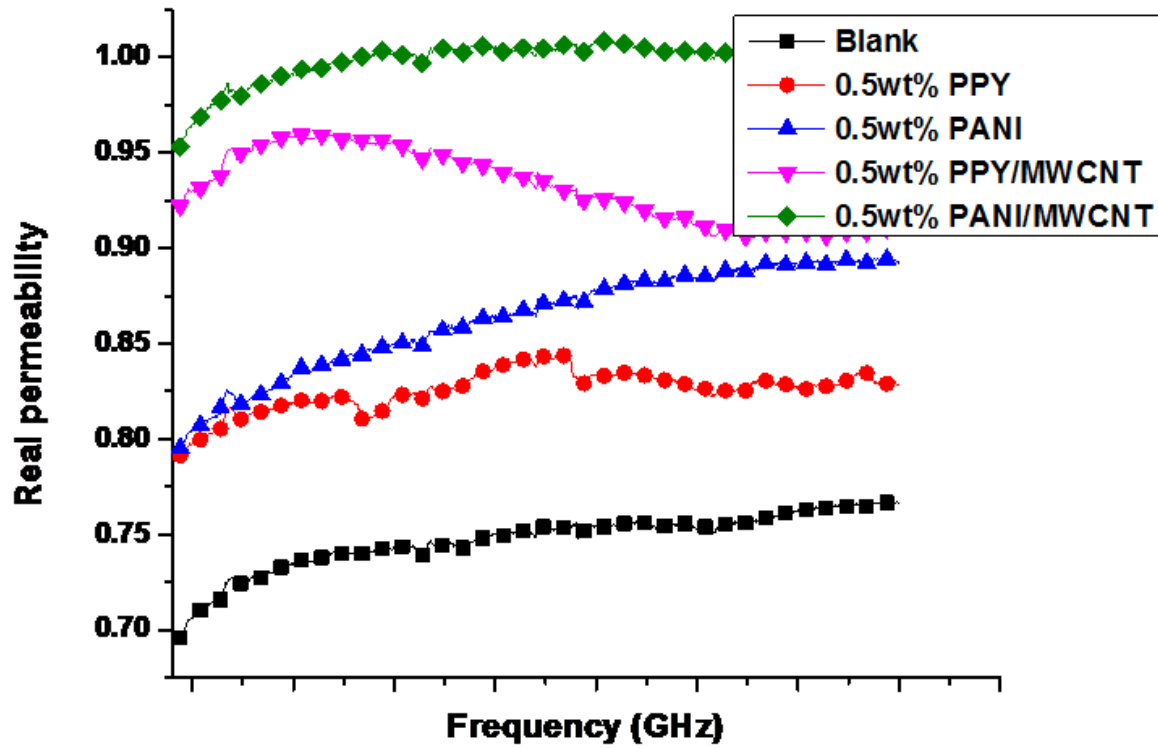


Fig.3.3.2.a. Real part of permeability of E-glass-epoxy composite at 0.5 wt% of CPs and CP/MWCNTs in X – band.

4. CONCLUSIONS

E-glass-epoxy composites were modified by using conducting polymers (PPY and PANI) (CPs) and MWCNTs enwrapped by CPs (CP/MWCNT) in order to increase the permittivity and permeability in the frequency range 8.2 GHz- 12.4 GHz. E-glass-epoxy composites having 0.5wt% of CP/MWCNT, exhibited highest permittivity than the individual CP reinforced E-glass-epoxy or control E-glass-epoxy composites. This can be attributed to the increased interfacial polarization by charge transport capability enabled by the π - π stacking interaction between MWCNTs and conducting polymer chains. Hence the composite material has great potential of application in the highly efficient thin microwave absorber.

5. REFERENCES

1. Nayak, N. V. (2014). Composite materials in aerospace applications. *International Journal of Scientific and Research Publications*, 4(9), 1-10.
2. Nanni, F., Travaglia, P., & Valentini, M. (2009). Effect of carbon nanofibres dispersion on the microwave absorbing properties of CNF/epoxy composites. *Composites science and technology*, 69(3), 485-490.
3. Huang, Y., Li, N., Ma, Y., Du, F., Li, F., He, X., ... & Chen, Y. (2007). The influence of single-walled carbon nanotube structure on the electromagnetic interference shielding efficiency of its epoxy composites. *Carbon*, 45(8), 1614-1621.
4. Qin, F., & Brosseau, C. (2012). A review and analysis of microwave absorption in polymer composites filled with carbonaceous particles. *Journal of applied physics*, 111(6), 061301.
5. Wang, Z., & Zhao, G. L. (2013). Microwave Absorption Properties of Carbon Nanotubes-Epoxy Composites in a Frequency Range of 2-20 GHz. *Open Journal of Composite Materials*, 3, 17-23.
6. Park, K. Y., Lee, S. E., Kim, C. G., & Han, J. H. (2006). Fabrication and electromagnetic characteristics of electromagnetic wave absorbing sandwich structures. *Composites science and technology*, 66(3), 576-584.
7. Wang, Y., & Jing, X. (2005). Intrinsically conducting polymers for electromagnetic interference shielding. *Polymers for advanced technologies*, 16(4), 344-351.
8. Lin, C. T., Swanson, B., Kolody, M., Sizemore, C., & Bahns, J. (2003). Nanograin magnetoresistive manganite coatings for EMI shielding against directed energy pulses. *Progress in organic coatings*, 47(3), 190-197.
9. Hoang, A. S., Nguyen, H. N., Bui, H. T., Tran, A. T., Duong, V. A., & Nguyen, V. B. (2013). Carbon nanotubes materials and their application to guarantee safety from exposure to electromagnetic fields. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 4(2), 025012.
10. Kumar, G. S., Vishnupriya, D., Joshi, A., Datar, S., & Patro, T. U. (2015). Electromagnetic interference shielding in 1–18 GHz frequency and electrical property correlations in poly (vinylidene fluoride)–multi-walled carbon nanotube composites. *Physical Chemistry Chemical Physics*, 17(31), 20347-20360.

11. Rao, G. A., & Mahulikar, S. P. (2002). Integrated review of stealth technology and its role in airpower. *Aeronautical Journal*, 106(1066), 629-641.
12. Oh, J. H., Oh, K. S., Kim, C. G., & Hong, C. S. (2004). Design of radar absorbing structures using glass/epoxy composite containing carbon black in X-band frequency ranges. *Composites Part B: Engineering*, 35(1), 49-56.
13. Micheli, D., Vricella, A., Pastore, R., & Marchetti, M. (2014). Synthesis and electromagnetic characterization of frequency selective radar absorbing materials using carbon nanopowders. *Carbon*, 77, 756-774.
14. Yang, S., Lozano, K., Lomeli, A., Foltz, H. D., & Jones, R. (2005). Electromagnetic interference shielding effectiveness of carbon nanofiber/LCP composites. *Composites Part A: applied science and manufacturing*, 36(5), 691-697.
15. Kumar, M. S., Raju, N. M. S., Sampath, P. S., & Jayakumari, L. S. (2014). EFFECTS OF NANOMATERIALS ON POLYMER COMPOSITES-AN EXPATIAATE VIEW. *Reviews on Advanced Materials Science*, 38(1), 40-54.
16. Li, N., Huang, Y., Du, F., He, X., Lin, X., Gao, H., ... & Eklund, P. C. (2006). Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano letters*, 6(6), 1141-1145.
17. Cao, M. S., Song, W. L., Hou, Z. L., Wen, B., & Yuan, J. (2010). The effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites. *Carbon*, 48(3), 788-796.
18. Zhao, D. L., Li, X., & Shen, Z. M. (2008). Electromagnetic and microwave absorbing properties of multi-walled carbon nanotubes filled with Ag nanowires. *Materials Science and Engineering: B*, 150(2), 105-110.
19. De Rosa, I. M., Dinescu, A., Sarasini, F., Sarto, M. S., & Tamburrano, A. (2010). Effect of short carbon fibers and MWCNTs on microwave absorbing properties of polyester composites containing nickel-coated carbon fibers. *Composites Science and Technology*, 70(1), 102-109.
20. Zhao, D. L., Li, X., & Shen, Z. M. (2008). Microwave absorbing property and complex permittivity and permeability of epoxy composites containing Ni-coated and Ag filled carbon nanotubes. *Composites Science and Technology*, 68(14), 2902-2908.

21. Hu, H., Zhao, Z., Zhou, Q., Gogotsi, Y., & Qiu, J. (2012). The role of microwave absorption on formation of graphene from graphite oxide. *Carbon*, 50(9), 3267-3273.
22. Chung, D. D. L. (2001). Electromagnetic interference shielding effectiveness of carbon materials. *carbon*, 39(2), 279-285.
23. Che, R., Peng, L. M., Duan, X. F., Chen, Q., & Liang, X. L. (2004). Microwave absorption enhancement and complex permittivity and permeability of Fe encapsulated within carbon nanotubes. *Advanced Materials*, 16(5), 401-405.
24. Li, N., Huang, Y., Du, F., He, X., Lin, X., Gao, H., ... & Eklund, P. C. (2006). Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano letters*, 6(6), 1141-1145.
25. Singh, A. P., Gupta, B. K., Mishra, M., Chandra, A., Mathur, R. B., & Dhawan, S. K. (2013). Multiwalled carbon nanotube/cement composites with exceptional electromagnetic interference shielding properties. *Carbon*, 56, 86-96.
26. Tyagi, S., Verma, P., Baskey, H. B., Agarwala, R. C., Agarwala, V., & Shami, T. C. (2012). Microwave absorption study of carbon nano tubes dispersed hard/soft ferrite nanocomposite. *Ceramics International*, 38(6), 4561-4571.
27. Duggal S., & Aul G. D. (2014). Review on Effect of Electric Permittivity and Magnetic Permeability over Microwave Absorbing Materials at Low Frequencies. *International Journal of Engineering and Advanced Technology*, 3(5), 12-19.
28. Wang, C., Han, X., Xu, P., Zhang, X., Du, Y., Hu, S., ... & Wang, X. (2011). The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material. *Applied Physics Letters*, 98(7), 072906.
29. Barber, P., Balasubramanian, S., Anguchamy, Y., Gong, S., Wibowo, A., Gao, H., ... & Zur Loye, H. C. (2009). Polymer composite and nanocomposite dielectric materials for pulse power energy storage. *Materials*, 2(4), 1697-1733.
30. Saini, P., & Arora, M. (2012). Microwave Absorption and EMI Shielding Behavior of Nanocomposites Based on 2 Intrinsically Conducting Polymers, 3 Graphene and Carbon Nanotubes 4.
31. Singh, B. P., Saket, D. K., Singh, A. P., Pati, S., Gupta, T. K., Singh, V. N., ... & Mathur, R. B. (2015). Microwave shielding properties of Co/Ni attached to single walled carbon nanotubes. *Journal of Materials Chemistry A*, 3(25), 13203-13209.

32. Krushnamurty, K., Rini, M., Srikanth, I., Ghosal, P., Das, A. P., Deepa, M., & Subrahmanyam, C. (2016). Conducting polymer coated graphene oxide reinforced C-epoxy composites for enhanced electrical conduction. *Composites Part A: Applied Science and Manufacturing*, 80, 237-243.
33. Saini, P., Choudhary, V., Singh, B. P., Mathur, R. B., & Dhawan, S. K. (2009). Polyaniline-MWCNT nanocomposites for microwave absorption and EMI shielding. *Materials Chemistry and Physics*, 113(2), 919-926.
34. Wang, C. H., Chen, C. C., Hsu, H. C., Du, H. Y., Chen, C. P., Hwang, J. Y., ... & Chen, K. H. (2009). Low methanol-permeable polyaniline/Nafion composite membrane for direct methanol fuel cells. *Journal of Power sources*, 190(2), 279-284
35. Hatui, G., Bhattacharya, P., Sahoo, S., Dhibar, S., & Das, C. K. (2014). Combined effect of expanded graphite and multiwall carbon nanotubes on the thermo mechanical, morphological as well as electrical conductivity of in situ bulk polymerized polystyrene composites. *Composites Part A: Applied Science and Manufacturing*, 56, 181-191.
36. Sahoo, N. G., Jung, Y. C., So, H. H., & Cho, J. W. (2007). Polypyrrole coated carbon nanotubes: synthesis, characterization, and enhanced electrical properties. *Synthetic Metals*, 157(8), 374-379.